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Analyses of the NMR Spectra of the Vinyl Protons of Cyclopentadiene
and Cyclohexadiene Using Spin Decoupling*

by

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Introduction

The proton n.m.r. spectra of heterocyclic five-membered ring dienes containing one oxygen^{1,2}, nitrogen², sulfur^{1,3} or selenium⁴ atom have been reported. We report here the analysis of the vinyl proton spectrum of cyclopentadiene (I) which has instead of a heteroatom an insulating methylene group between the 1- and 4-position of the cis-diene. The analysis was accomplished using double and triple irradiation techniques.

To our knowledge there is no previous report of the n.m.r. parameters for a six-membered ring cis-1,3-diene. Using proton-proton decoupling we were able to simplify the vinyl proton region of cyclohexadiene (II) to an analyzable A₂B₂ spectrum. The molecule II may approximate a model for cis-1,3-butadiene and as such its n.m.r. coupling constants could indicate something about the electronic structure of cis-dienes.

The n.m.r. parameters for I and II are discussed in terms of the mechanisms of long-range proton-proton couplings, effects of ring size, and the relative signs of the various spin-spin couplings.

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Experimental

Spectra were obtained with a Varian HR-60 spectrometer modified with a nuclear magnetic resonance field-frequency stabilizer similar to that described by Freeman and Anderson⁵. This particular system incorporated two phase detectors of the same design as described by us previously⁶. When performing multiple resonance experiments it was found desirable to use a General Radio narrow band sound analyzer, GR 1554A, at the 1000 cps locking frequency. A more detailed description of the complete system is given elsewhere⁷. Spectra were recorded by frequency sweep in most uses.

Cyclopentadiene (I) was obtained by cracking the dimer. Cyclohexadiene (II) was a commercial sample and contained an impurity of cyclohexene. About 7-10% tetramethylsilane was added to each sample in Varian thin-walled 5 mm sample tubes. Oxygen was removed by bubbling nitrogen through the samples for about three minutes.

Results

The complete analyses of the proton n.m.r. spectra of I and II present rather formidable tasks as is evident from observation of the complexities of the vinyl proton regions for these molecules (see fig. 1a and fig. 3a, respectively). In the case of I the great multiplicity of lines and the fact that ring obscures the true positions of nearly all of the vinyl resonance lines make a straight forward iterative approach to the analysis of this spectrum rather unattractive.

By placing a large-field modulation at the methylene proton frequency in a frequency-sweep experiment we were able to bring about a rather gratifying simplification of the vinyl proton region of I to an A_2B_2 system as shown in fig. 1b. Fig. 1c shows similar though less pleasing results obtained in a field-sweep experiment. From several spectra of the

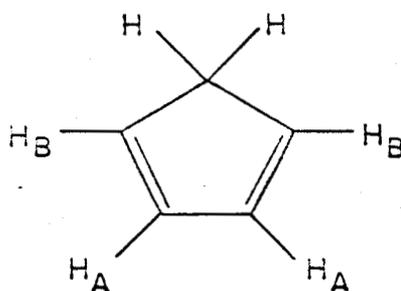
quality of fig. 1b it was possible to obtain line position measurements accurate to ± 0.01 cps.

To the decoupled spectrum of I it was possible to introduce a second perturbing field-modulation at various lines of the A_2B_2 system. Two examples of these triple irradiation experiments are shown in figs. 2b and 2c. These triple irradiation experiments demonstrated that lines 4, 7, 14 and 17 (as labeled in fig. 2a) were related to each other. These transitions are the antisymmetrical ones and each is doubly degenerate. The identity of symmetric transitions follows immediately. From consideration of the number of other lines split when each line was irradiated the specific assignment based on the usual notation for the A_2B_2 spin system¹ could be made and is summarized below:

Line	Assignment ¹
1	5
2	1
3	2
4	9,10
5	6
6	7
7	11,12
8	3
9	4
10	8

A final set of parameters was obtained using the Swalen and Reiley NMRIT program⁸:

δ_{AB}	8.079 ± 0.004 cps
J_{AA}	$+1.944 \pm 0.007$
J'_{AB}	$+1.090 \pm 0.006$
J_{AB}	$+5.064 \pm 0.006$
J_{BB}	$+1.944 \pm 0.006$



The average deviation between observed and calculated line positions was 0.008 cps.

As shown in fig. 3b we were able to simplify the vinyl proton spectrum of II to an A_2B_2 system but the results were not nearly as good as those obtained for I. Because the methylene proton frequency was close to 120 cps from the tetramethylsilane frequency enough modulation was present close to this latter frequency when a large modulation was placed at the former frequency to cause saturation of the locking signal and serious beats in the locking loop. Both of these factors, which we could not remove, tended to unlock the spectrometer while the spectrum of II was being swept with a modulation level at the methylene proton frequency sufficient to achieve the desired amount of decoupling. Despite these difficulties it was possible to obtain rather satisfactory spectra of one side of the A_2B_2 spectrum of II and in several cases complete spectra were swept through without the spectrometer unlocking. Data from these spectra gave a set of line position measurements accurate to ± 0.05 cps.

We were not at all able to introduce a second large perturbing field into the decoupled spectrum of II to trace out the energy of the A_2B_2 system without immediately unlocking the spectrometer. An assignment of the A_2B_2 spectrum of II was started by recognizing a certain similarity between the spectrum of II and certain A_2B_2 spectra of *o*-disubstituted benzene recently discussed by Grant et al.¹ As discussed by the latter

authors values of N and L and thus the chemical shift were obtained from certain repetitive spacing in the spectrum of the A_2B_2 system of II. Trial assignments for the various relative sign assignments between the long-range H-C=C-C=C-H and H-C=C-C-H couplings were considered. The only assignment which gave a satisfactory convergence for NMRIT and which gave agreement with experimental intensities and satisfactory agreement with line positions was that given below:

δ_{AB}	6.394 ± 0.013
J_{AA}	$+5.142 \pm 0.028$
J'_{AB}	$+1.064 \pm 0.027$
J_{AB}	$+9.417 \pm 0.033$
J_{BB}	$+1.944 \pm 0.028$

The average deviation between observed and calculated line positions was 0.089. The much larger errors in the analysis of the A_2B_2 spectrum of II we attribute to incomplete decoupling which resulted in certain of the A_2B_2 lines being shifted from their true position. The difference between one pair of observed and calculated lines was 0.24 cps (lines 7 and 7').

Analyses of the A_2B_2 spectra for the vinyl protons of I and II does not determine whether the A or B protons are upfield in these molecules and in fact the assignment of some of the coupling constants is based on analogy to other molecules¹. However, a determination of which set of vinyl protons in I and II are adjacent to methylene groups can be made.

An assignment of the upfield vinyl protons as those adjacent to the methylene group for II was based on the fact that this group of vinyl protons is more strongly coupled to the methylene protons as evidenced from the uncoupled spectrum (see fig. 3a). In the case of the latter protons we expect a positive coupling of about 3-4 cps and in the case of the down-

field vinyl protons a negative coupling of about 1-2 cps as estimated from data for the cycloolefins⁹.

In our previous reported analysis of the spectrum of indene⁶, which contains a methylene group adjacent to two double bonds and part of a five-membered ring and which should be closely analogous to I, we found that in the five-membered ring the H-C-C=C-H coupling was a different sign than the H-C=C-H and H-C-C-H couplings, which are both presumed to be positive in sign^{10,11}. The complete proton spectrum of I is a $A_2B_2X_2$ spectrum and J_{AX} and J_{BX} are only slightly different. In the undecoupled spectrum of the vinyl proton each line of the decoupled A_2B_2 spectrum should be split into 1:2:1 triplets. The methylene protons of I give a quintet to first order. On selective irradiation of the low-field member of the methylene quintet we should be irradiating transitions having one set of the vinyl protons in spin state $\alpha\alpha$ and the other set in spin state $\beta\beta$ reasoning from the results for indene⁶.

From detailed consideration of the spin states of the various lines of the A_2B_2 decoupled spectrum we would expect in the experiment described above to see perturbation in the downfield portion of the half of the vinyl proton spectrum assignable to the protons with the negative long-range H-C-C=C-H coupling and some perturbation in the upfield portion of the half of the vinyl proton spectrum assignable to the vinyl protons adjacent to the methylene group. Reasoning in this manner the results from the experiment indicated that the upfield vinyl protons were those adjacent to the methylene group. An additional experiment where the upfield member of the methylene quintet was irradiated confirmed this result. These results will be described in more detail elsewhere.

Discussion

Recently there has been considerable interest in the nature of long-range proton-proton spin-spin couplings. We define "long-range" couplings as those existing between protons more than three bonds apart (i.e. 4J 's and 5J 's, where the superscript denotes the number of chemical bonds separating coupled nuclei). At present several possible mechanisms have been postulated for these couplings. In saturated molecules 4J coupling is thought to be transmitted through the σ -bond framework just as the vicinal 3J coupling¹². In addition there is some evidence that 4J and 5J coupling can be transmitted through space if the intra-proton distances are small enough¹³. In unsaturated molecules both of these mechanisms could be important in addition to a contribution transmitted through the π -electron system¹⁴. This π -electron mechanism involving σ - π configuration interaction is usually the largest contribution to long-range couplings in conjugated molecules. The results for I and II reported here combined with some other recent results on trans-1,3-dienes^{15, 16, 17} provide some information on the relative importances of these mechanisms.

In Table I are given data for several open chain trans-dienes. In these molecules there are several 4J 's and 5J 's. The theory of the propagation of spin-spin coupling through a π -electron system¹⁴ predicts that the coupling will be positive when a pair of protons are separated by an odd number of bonds and negative when they are separated by an even number of bonds. The sign results for the 4J 's and 5J 's for the trans-1,3-butadienes are in agreement with the theory. In the case of I and II both these types of long-range couplings are found to be positive.

If the values for the 4J 's of 1,3-butadiene of about -0.8 cps are taken to be characteristic of this π -contribution in dienes then in I and II the measured 4J 's (not considering J_{BB} in I for the moment) must

be the sum of a -0.8 cps π -contribution and a $+1.9$ cps contribution from other mechanisms. The usual σ -contribution to 4J 's appears to be about 0.1 to 0.3 cps¹³ or considerably less in magnitude than this 1.9 cps contribution. The protons involved in I and II are rather distant from each other when compared with other molecules in which a through-space contribution to 4J is believed to exist because of closely disposed protons¹³. Long-range couplings in the range of a positive $1-2$ cps have been observed in saturated molecules when the angular disposition between the two C-H bonds in a H-C-C-C-H fragment is similar to that found in I and II¹³ even though the intra-proton distance is relatively great i.e. greater than about 3 \AA . We ascribe the magnitudes of the 4J 's (excluding J_{BB} in I) in I and II as arising from a $+1.9$ cps contribution from a coupling mechanism which is significant when the angular disposition of the C-H bonds is such that lines through these bonds will nearly cross somewhere behind the carbon atoms to give an angle in the range of $90-180^\circ$. This kind of coupling mechanism is probably the same one responsible for the very large ($3-14$ cps) 4J 's observed in some bridged ring systems¹³; if this is the case then it is likely that these large couplings are also positive.

The J_{BB} in I, which is a 4J , although coupling via the π -electron would involve 5J , and the 5J in II are about 1 cps different from each other and both positive. It has been estimated that the 5J π -coupling will be about $+0.7$ cps¹⁴. Although it would be expected that this π -coupling should be independent of orientation for a butadiene and depend on the π -bond order between the coupled protons, experimental evidence shows that ${}^5J_{tt}$ (the 5J between 1,4-protons each trans to the formal single bond of a trans-1,3-diene) is about twice as large as the other 5J 's (i.e. ${}^5J_{cc}$ and J_{tc})^{16,17}. The ${}^5J_{cc}$ and ${}^5J_{tt}$ for trans-1,3-dienes are in the range of $+0.5$ to $+0.8$ cps which is in rather close agreement with the theory. If

we assume that effects present in the ${}^5J_{tt}$ couplings in trans-dienes are absent in the case of I and II then the observed magnitudes of J_{BB} in I and the 5J in II can be explained as arising from +0.7 cps π -contributions and +1.2 cps and +0.2 cps contributions, respectively, from other mechanisms. A 4J σ -contribution to J_{BB} of I through the methylene group should be small (i.e. 0.1-0.3 cps)¹³. The angular disposition between the C-H bonds involving the B protons of I is similar to that for the protons involved in the other 4J 's in this molecule, which were discussed above, except that the intra-carbon distance is slightly larger here. If a similar cross-ring through-space mechanism is again operative it is about +1.2 cps in magnitude, possibly reflecting the slightly larger intra-carbon distance in this case. Assuming that this same mechanism is present in II, the much smaller contribution of +0.2 cps to 5J again probably reflects mainly the significantly greater intra-carbon distance. The magnitudes and signs of the 4J 's and 5J 's in II are very similar to those found in o-disubstituted benzenes¹ which are most certainly related to the similar geometry and suggest that similar coupling mechanisms are operative in both types of ring compounds.

The cis-vinylic couplings in 1,3-butadiene is +10.17 cps and that in II is +9.42 cps which shows that the electronic structure in these two types of double bonds is only slightly different. The much smaller value of +5.06 cps in I apparently reflects the effect of ring contraction on vicinal coupling as has been observed when going from a six- to a five-membered ring⁹. The values of J_{AA} for I and II, +1.94 cps and +5.14 cps, respectively, reflect this same effect. The ratio of the trans- to cis-vinylic couplings in 1,3-butadiene is about 1.7 while the ratio of the trans-coupling between protons on the formal single bond of butadiene to the corresponding cis-coupling in II is 1.8. This result may indicate that

there is a close electronic similarity in the structure of the two formal single bonds in butadiene and II and also in general the same terms determine the coupling between vicinal protons separated by two sp^2 carbon atoms except for a scale factor which may be related to the π -bond order*. That such a relation exists may be indicated from the observation of the parallelism between the sum of the two vicinal couplings in II which is 14.6 cps and in naphthalene which is 14.6 cps¹⁸ and the sums of the corresponding π -bond order for the two adjacent bonds of 1.34 and 1.33, respectively, as calculated by the molecular orbital method¹⁹. This comparison would not seem to support the recent contentions of Dewar and Schmeising¹⁹ that appreciable conjugation does not exist in unsaturated systems such as 1,3-dienes.

The analyses of the complete spectra of I and II are in progress and will be reported subsequently.

* The couplings in II will embody certain steric effects characteristic of six-membered rings which allow more useful comparison to couplings in benzene derivatives. These steric effects probably account for the slight difference of the cis-vinylic couplings between butadiene and II.

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Table I. Coupling Constants for I, II and Some 1,3-butadienes

	3J_t	3J_c	2J	$^3J_{2,3}$	4J_c	4J_t	$^5J_{tt}$	$^5J_{cc}$	$^5J_{tc}$	ref.
I		+5.06		+1.94		+1.09		+1.94		
II		+9.42		+5.14		+1.06		+0.91		
1,3-Butadiene	+17.05	+10.17	+1.74	+10.41	-0.83	-0.86	+1.30	+0.69	+0.60	17
2-t-Butyl-1,3-butadiene	+17.00	+10.80	+2.30 (4,4')	--	±1.00	±0.40	a l l	$^5J_{ts}$	z e r o	17
			+1.70 (1,1')							
trans,trans-1,4-Diphenyl-1,3-butadiene	+15.62	--	--	+10.80	-0.94	--	--	+0.90	--	16
cis,trans-1,4-Dichloro-1,3-butadiene	+13.34	+7.24	--	+10.84	-1.19	-0.71	--	--	+0.76	16

Fig. 1. Spectrum of the vinyl protons of cyclopentadiene (I) at 60 Mc.

(a) Uncoupled and frequency swept. (b) Decoupled from methylene protons and frequency swept. (c) Same as (b) except field swept.

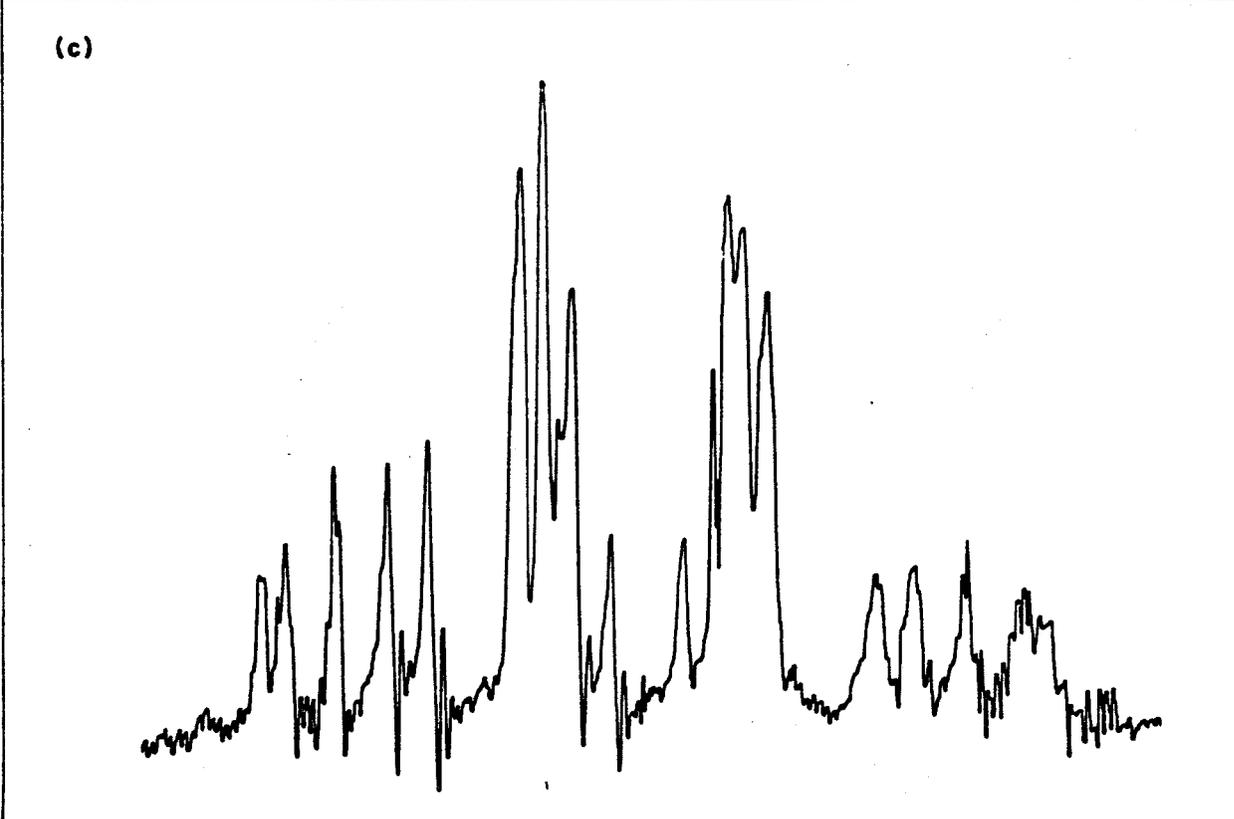
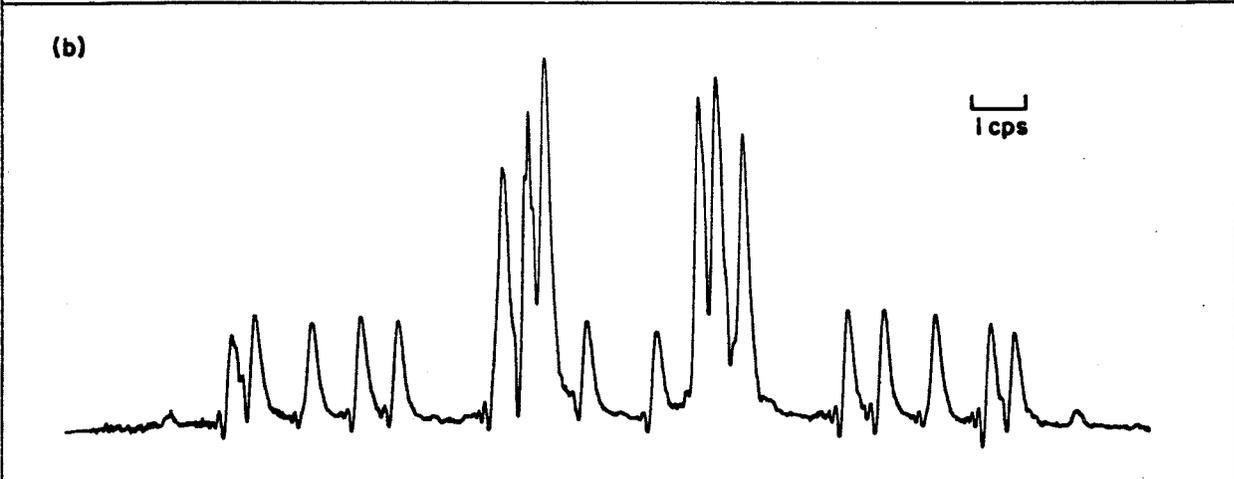
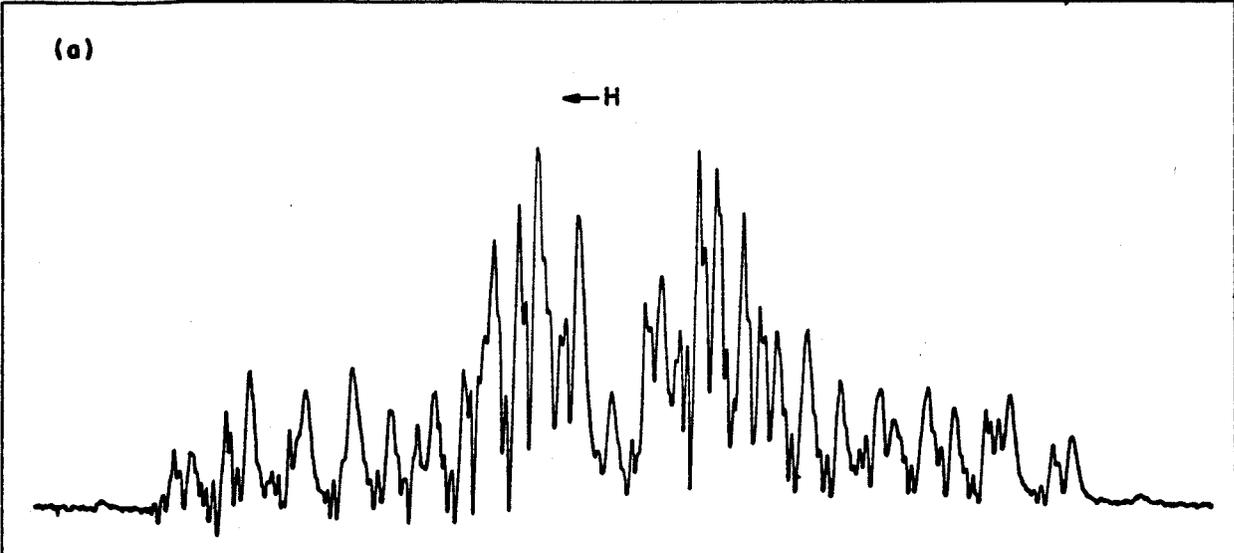
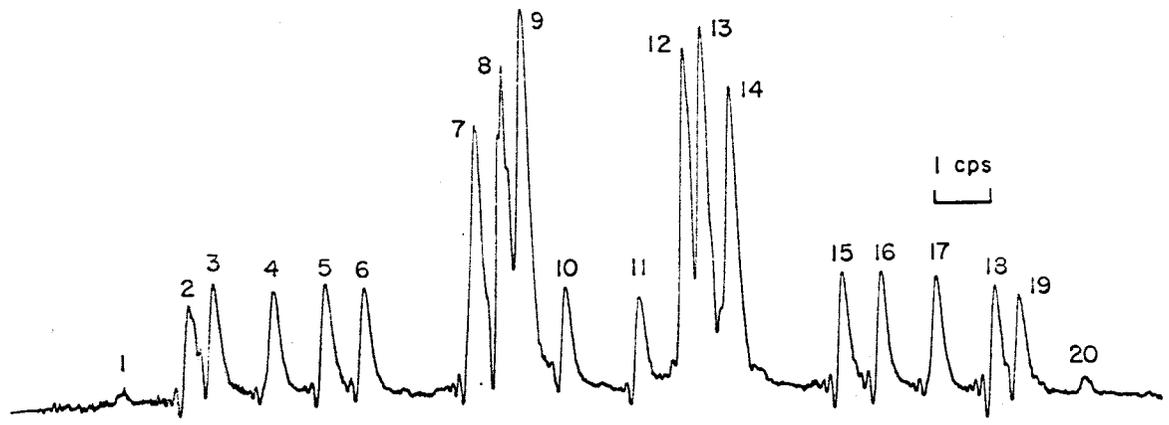


Fig. 2. Spectrum of the vinyl protons of cyclopentadiene (I) at 60 Mc.

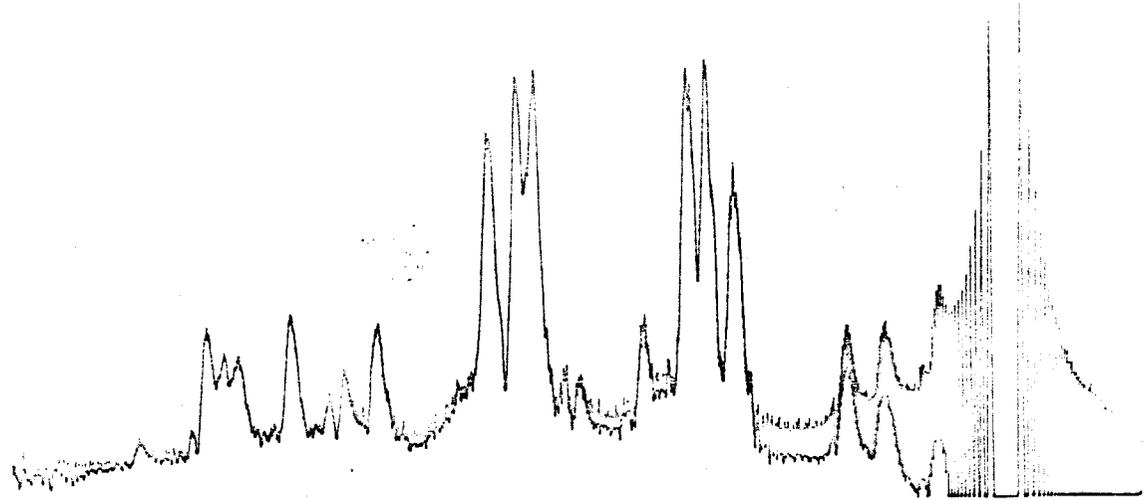
(a) Decoupled from methylene protons and frequency swept.

(b) Same as (a) in addition to irradiation of line 18. (c) Same as (a) in addition to irradiation of line 17.

(a)



(b)



(c)

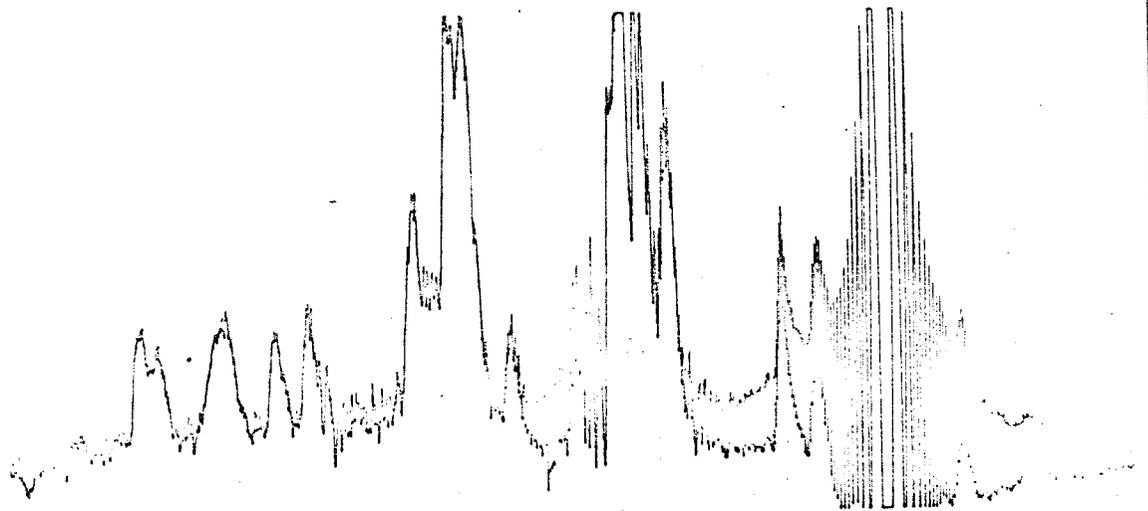


Fig. 3. Spectrum of the vinyl protons of cyclohexadiene (II) at 60 Mc.
(a) Undecoupled and frequency swept. (b) Decoupled from methylene protons and frequency swept. Transitions labeled according to the usual convention for A_2B_2 spin systems; see ref. 1.

